Self-Study / Tutorial / Exam Preparation Problems

- Identify the possible term symbols that can arise from the configuration $2p^1 3p^1$
    - first identify the possible L and S values:
    - we know $l_1=1$, $l_2=1$ thus max $L= l_1+l_2=2$ thus possible L=2, 1, 0, we have potential D, P, S terms
    - we know $s_1=1/2$, $s_2=1/2$ thus max $S= s_1+s_2=1$ thus possible S=1, 0, we have potential multiplicity of 3 and 1
    - thus we have potential ^3D, ^1D, ^3P, ^1P, ^3S, ^1S terms
    - possible values of J are J=L+S, L+S-1, ... |L-S|

L, S	L+S, L+S-1, ... |L-S|	J	term symbol
L=2 S=1	2+1, 2+1-1, ...|2-1|	3, 2, 1	$^3D_3$, $^3D_2$, $^3D_1$
L=2 S=0	2+0, 2+0-1, ...|2-0|	2	$^1D_2$
L=1 S=1	1+1, 1+1-1, ...|1-1|	2, 1, 0	$^3P_2$, $^3P_1$, $^3P_0$
L=1 S=0	1+0, 1+0-1, ...|1-0|	1	$^1P_1$
L=0 S=1	0+1, 0+1-1, ...|0-1|	1, 0	$^3S_1$, $^3S_0$
L=0 S=0	0+0, 0+0-1, ...|0-0|	0	$^1S_0$

    - thus the complete list of potential term symbols is $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$, $^3S_1$, $^3S_0$ and $^1S_0$
    - all of these terms are allowed because the pAOs are different, however in the notes we considered the equivalent of $2p^2$ or $3p^2$, in this case some of the terms are not allowed due to Hund's rules or some non-intuitive quantum mechanical accounting.
    - the first thing to note is that the ^3D terms are not allowed, this requires $L= l_1+l_2=2$ and $S= s_1+s_2=1$ with the associated M_L=-2, -1, 0, 1, 2 and M_S=-1, 0, 1 values available. For $M_L=2$ this requires $m_{l(1)}=+1$ and $m_{l(2)}=+1$ ie both electrons in the same orbital and since $M_S=1$ requires $m_{s(1)}=+1/2$ and $m_{s(2)}=+1/2$ both electrons cannot have the same quantum numbers (Pauli principle) and this entire set of microstates is not allowed.
    - however assessing the remaining term symbols is more complex and the best way to proceed is via a table of M_L and M_S values. We will consider ^1P. We will use a notation for electrons (1, 2) represented by $(m_{l(1)}, \bar{m}_{l(2)})$ m_l values with a bar representing spin of -1/2 (and no bar a spin of +1/2)

M_L, M_S	+1	0	-1
+2	X	$(1,\bar{1})$	X
+1	$(1,0)$	$(1,\bar{0})$ $(\bar{1},0)$	$(\bar{1},\bar{0})$
0	$(1,-1)$ X	$(1,-\bar{1})$ $(\bar{1},-1)$ $(0,\bar{0})$	$(\bar{1},-\bar{1})$ X
-1	$(-1,0)$	$(-1,\bar{0})$ $(-\bar{1},0)$	$(-\bar{1},\bar{0})$
-2	X	$(-1,-\bar{1})$	X

    - note that the Pauli principle applies to the M_L=+2 and -2 configurations with the same spin on both electrons (M_S=+1 or -1), denoted with an X. The same is true for $M_L=0$ if $m_{l(1)}=0$ and $m_{l(2)}=0$, but not the case if $m_{l(1)}=+1$ and $m_{l(2)}=-1$.
    - now one analyses these microstates to extract the relevant term symbols

- the microstate $(1,\bar{1})$ must belong to L=2, S=0 since $m_{l(1)}=1$ and $m_{l(2)}=1$ and identifies it as the ^1D term. There must be M_L values =-2, -1 ,0 ,1 ,2 and so we can cross out one each of the microstates on each of these rows. It doesn't matter which ones we eliminate as this is only a book keeping exercise.
- looking at the next row there is a microstate (1,0) in $M_L=1$ and $M_S=1$, this belongs to L=1, S=1 since $m_{l(1)}=1$ and $m_{l(2)}=0$ and identifies it as the ^3P term. L=1 has M_L=-1,0,1 and S=1 has Ms=-1,0,1 so we eliminate one microstate from each of these boxes in the table, removing 9 microstates.
- only one microstate remains, $(0,\bar{0})$ in $M_L=0$ and $M_S=0$, this belongs to L=0, S=0 and identifies the ^1S term.
- thus of the complete set of potential term symbols is $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$, $^3S_1$, $^3S_0$ and $^1S_0$ the p^2 configuration allows only $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$ and $^1S_0$.

- Determine the full ground state term symbol for a d^3 free ion configuration (using Hund's rules and determining possible J values), what is the degeneracy of this state?
  - Hund's rules state that the ground state has the highest multiplicity
  - therefor all the electrons will be unpaired and S=3/2 thus multiplicity=2(3/2)+1=4
  - for dAOs l=2 thus m_l=-2, -1, 0, 1, 2 and the maximum (summed) M_L=2+1+0=3 (since e's cannot have the same quantum numbers each one must have a different m_l given the l=2 for all the electrons)
  - if the maximum $M_L=3$ then the maximum L=3 this has the term symbol F
  - the J values have a maximum J=L+S, therefore the max J value is J=3+3/2=6/2+3/2=9/2
  - then J values vary as (L+S), (L+S-1)...|L-S| so J=9/2, 7/2, 5/2 and 3/2 (since L-S=3/2).
  - each J has degeneracy of 2J+1 so J=9/2 has 10 M_J values, J=7/2 has 8 M_J values, J=5/2 has 6 M_J values, J=3/2 has 4 M_J values giving a a total degeneracy of 10+8+6+4=28
  - thus the lowest energy d^3 state has term symbol ^4F and this level has 4 sublevels $^4F_{9/2}$(10), $^4F_{7/2}$(8), $^4F_{5/2}$(6) and $^4F_{3/2}$(4), where the degeneracy of each level is given in brackets
- How many transitions should be expected for each of the d^1 to d^8 configurations?
  - using the Orgel diagrams we should expect a single transition for all d^1, d^4, d^6 and d^9 complexes and three transitions for all d^2, d^3, d^7 and d^8 complexes
  - high spin d^5 complexes are a special case as any transitions will require a spin change, thus no transitions are expected and d^5 complexes tend to be very weakly coloured.
- Why is $[Ti(H_2O)_6]^{3+}$ violet?
  - Ti is group 4 d^4, H_2O is a neutral ligand while the charge removes 3e this is a Ti d^1 complex.
  - there is no Tanabe-Sugano diagram for d^1 as this configuration has only a single free ion electronic state ^2D which is splits into the $^2T_{2g}$ and ^2E_g states in the strong field limit
  - thus the $^2T_{2g}$ state is the ground state

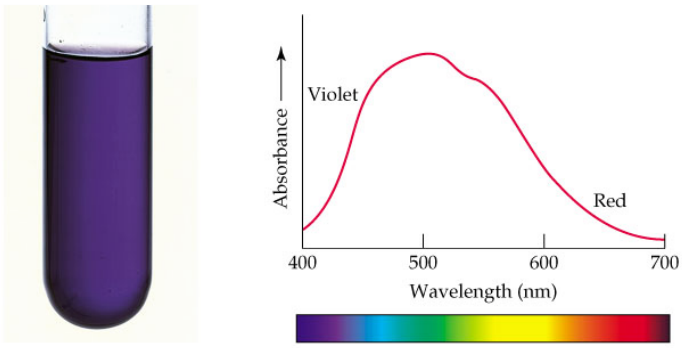

Figure 1 solution and spectrum of $[Ti(H_2O)_6]^{3+}$.[1]

- only a single excitation is possible from $(t_{2g})^1$ to $(e_g)^1$ thus the excited state has ^2E_g symmetry, this also means the transition is going to reflect very closely the Δ_{oct}.
- the transition will be angular momentum forbidden (Δl=0) and parity forbidden (as the initial and final states are both g) but as there is colour a a transition must be occurring
- $[Ti(H_2O)_6]^{3+}$ absorbs at ≈ 20,300cm_{-1} or ≈500nm which is in the blue-green region letting the red-violet light through
- we have partially occupied degenerate levels in both the ground and excited state, thus a Jahn-Teller distortion can occur (vibronic coupling), the associated symmetry breaking will lead to a formally forbidden mode gaining intensity and leading to a broad absorbtion.

[1] downloaded from http://wps.prenhall.com/wps/media/objects/4680/4793024/ch20_10.htm, 23 Feb 2015